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USE OF SPREADSHEETS IN THERMAL ANALYSIS. PART 5

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ABSTRACT

Spreadsheet analysis of non-isothermal TG (NITG) data has recently been successfully applied to various organic and inorganic materials using various algorithms.

In this paper, this type of analysis will now be applied to isothermal TG (ITG) data. An algorithm will be tested for ITG data which is a modification of one which has been successfully utilized for NITG data.

The aim of this paper is to extend the utilization of spreadsheet analysis to the estimation of kinetic parameters from both theoretical and experimental ITG data.

INTRODUCTION

Spreadsheet analysis of non-isothermal TG (NITG) data has recently been successfully applied to various materials using various algorithms [1–4]. In this manner, the values of various kinetic parameters, such as reaction order, n, and activation energy, E, were obtained, as well as the mechanism. Also, various commercial spreadsheets have been briefly described along with some of their advantages and disadvantages when applied to thermal analysis.

In this paper, this type of analysis will now be applied to isothermal TG (ITG) data. Thus, isothermal theoretical and isothermal experimental reaction data will be utilized. An algorithm will be employed for the ITG data which is a modification of one which has been successfully employed for NITG data [1,5]. The reason for this algorithm modification will be elaborated upon below.

The ultimate aim of this paper is to extend the utilization of spreadsheets to the estimation of kinetic parameters from ITG data which may be obtained from TG, DTA, and DSC, as well as from other instrumentation. In this connection, it may be mentioned that spreadsheet analyses were carried out using Lotus 1-2-3, Release 2.

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SOME THEORETICAL ASPECTS

For an n-order unimolecular or pseudo-unimolecular reaction which is related to ITG, we can obtain

$$1-(1-\alpha)^{(1-n)}=k(1-n)t \tag{1}$$

where α is the degree of conversion, k is a reaction rate constant, and t is the reaction time. Equation (1) may be expressed symbolically as

$$Y=mX+0 \tag{2}$$

Various values of $k(1-n)$ can be obtained for various particular n values by employing various pairs of α–t values and a least-squares procedure (LSQ). The LSQ which afforded an intercept closest to a value of zero yielded what was considered to be the most probable values for n and k, cf. eqn. (2).

RESULTS AND DISCUSSION

The particular spreadsheet algorithm adopted for the analysis of NITG data [1] was initially applied to the ITG data to be presented utilizing eqns. (1) and (2). It was found that although this algorithm had been successfully applied to NITG data for various materials, it was not always successful for ITG data and therefore required modification. A brief description of the NITG algorithm follows. In the NITG algorithm, it was assumed that as the most probable value (MPV) of n was exceeded, the LSQ intercept would change sign (e.g. from positive to negative). While this appears to be true for all the NITG data examined, this may not always hold for ITG data under the conditions in which n is incremented. Thus, the value of n is initially incremented by 0.1 and even though the intercept sign may change at, say, 0.85, it will not be picked up by the computer if values of intercepts at values of n of 0.8, 0.9, 1.0, etc., afford positive values of intercepts (there is no change of sign). In order to clarify the preceding further, consider the data in Tables 1 and 2. The following values of n, AAA1 (intercept), and AAA2 (slope) were obtained, respectively, from the Table 1 ITG data: 0.50, 0.0158, 0.00941; 0.60, 0.0054, 0.00822; 0.70, −0.0023, 0.00677; 0.80, −0.0066, 0.00497. From the preceding, it can be observed that as the MPV of $n(0.67)$ was exceeded, the sign of AAA1 changed, as anticipated. However, the ITG data from Table 2 yielded the following values for n, AAA1, and AAA2, respectively: 0.9, 0.00543, 0.00154; 1.00001, 2.21E − 7, −1.8E − 7; 1.1, 0.0122, −0.00212; 1.2, 0.0508, −0.00505. From the preceding, as the MPV of $n(1.0)$ was exceeded, the sign of AAA1 did not change. Thus, in this case, the algorithm was no longer valid. Modification of this particular spreadsheet algorithm was therefore undertaken and is described below.

TABLE 1

Spreadsheet analysis of isothermal theoretical data [6]

```
      A        B        C         D            E          F        Range
 1    Alpha X(Time)     N         Y            X*X        X*Y      Name       Cell(s)
 2 ==============================================================  ==================
 3    0.203     10.0  0.665    7.32E-02    1.00E+02 0.7319463   AAA1       B15
 4    0.377     20.0           1.47E-01    4.00E+02 2.9319663   AAA2       A15
 5    0.523     30.0           2.20E-01    9.00E+02 6.5887333   BX0        D15
 6    0.645     40.0           2.93E-01    1.60E+03 11.726049   INC        F15
 7    0.743     50.0           3.66E-01    2.50E+03 18.282598   N          C3
 8    0.822     60.0           4.39E-01    3.60E+03 26.345592   SX         B11
 9    0.883     70.0           5.13E-01    4.90E+03 35.885398   SXX        E11
10 ==============================================================  SXY        F11
11 TOTALS==>    280.0          2.05E+00    1.40E+04  1.02E+02   SY         D11
12 ==============================================================  VALS       A27
13   AAA2      AAA1                BX0                 Inc      X          B3..B10
14 ==============================================================  XX         E3..E10
15  7.32E-03 0.000048          4.86E-05               0.0001    XY         F3..F10
16 --------------------------------------------------------------  Y          D3..D10
17      \a--> {let n,0.1}~{let inc,0.1}~                         \A         B17
18            {let bx0,100}~                                     \B         B22
19      \d--> {goto}n~{let n,+n+inc}~                            \D         B19
20            {if @abs(+aaa1)<@abs(bx0)}{let bx0,aaa1}~{branch \d}
21            {branch \b}
22      \b--> {goto}n~{let n,+n-2*inc}~{let bx0,aaa1}~
23            {goto}inc~{let inc,+inc/10}~
24            {if +inc>.0009}{branch \d}
25            {goto}vals~
26
27 Final values n & k =>          0.665     2.19E-02
```

The following alterations of the algorithm were made, see Table 1. A cell named BX0 was introduced which contained previously obtained values of AAA1, cf. line A20. As long as absolute values of AAA1 were less than absolute values in BX0, the spreadsheet run continued normally. However, when this condition was no longer true (regardless of whether or not there involved a sign change), branching occurred as depicted in line A21. Then, the value of n was reduced by $2 \times$ inc so that the value of AAA1 remained positive and above, but close to, a value of zero. The content of BX0 now assumed this value of AAA1, cf. A22, and the run was continued via A23 and A24. This modified ITG spreadsheet algorithm was successfully applied to ITG theoretical and experimental data, as mentioned below.

Table 1 shows a spreadsheet analysis of ITG theoretical data (after final values were obtained). The final values of n and k were found to be, respectively, 0.665 and 0.0219 (compare $\frac{2}{3}$ and 0.022 in ref. 6). In this table, range names and corresponding cells are also depicted. In addition, in Table 3, there is a listing of the cell contents for the worksheet in Table 1.

TABLE 2

Spreadsheet analysis of isothermal experimental data [7]

```
      A          B        C        D           E          F
1     Alpha X(Time)       N        Y           X*X        X*Y
2 ===========================================================
3     0.340      24.4  0.973    1.12E-02    5.95E+02 0.2722117
4     0.453      35.0           1.62E-02    1.23E+03 0.5655062
5     0.567      48.0           2.23E-02    2.30E+03 1.0726088
6     0.680      64.8           3.03E-02    4.20E+03 1.9632007
7     0.737      75.8           3.54E-02    5.75E+03 2.6847430
8     0.793      89.4           4.16E-02    7.99E+03 3.7221187
9     0.850     106.6           4.99E-02    1.14E+04 5.3228040
10    0.907     133.4           6.21E-02    1.78E+04 8.2862995
11    0.963     183.6           8.52E-02    3.37E+04 15.636806
12 ==========================================================
13 TOTALS==>    761.0           3.54E-01    8.49E+04  3.95E+01
14 ==========================================================
15   AAA2     AAA1                 BX0                 Inc
16 ==========================================================
17  4.65E-04 0.000017            1.73E-05              0.0001
18 ----------    ---------------------------------------------
19     \a--> {let n,0.1}~{let inc,0.1}~
20           {let bx0,100}~
21     \d--> {goto}n~{let n,+n+inc}~
22           {if @abs(+aaa1)<@abs(bx0)}{let bx0,aaa1}~{branch \d}
23           {branch \b}
24     \b--> {goto}n~{let n,+n-2*inc}~{let bx0,aaa1}~
25           {goto}inc~{let inc,+inc/10}~
26           {if +inc>.0009}{branch \d}
27           {goto}vals~
28
29 Final values n & k =>            0.973     1.72E-02
```

Table 2 shows a spreadsheet analysis of ITG experimental data. Final values of n and k obtained were, respectively, 0.973 and 0.0172 (compare 0.97 and 0.0172 in ref. 7).

Additional ITG theoretical data [8] was analyzed via spreadsheet for values of n and k. Analysis by the unmodified algorithm was found to be unsuccessful for the α–t data used since as the MPV of n was exceeded, the value of AAA1 did not change sign. However, the modified algorithm described previously yielded the following values of n and k, respectively: 0.998 and 0.00674 (compare 1.0 and 0.0066 in ref. 8). Additional ITG experimental data [9] was also examined and afforded the following values of n and k, respectively: 0.998 and 0.00796 (compare 1.0 and 0.00796 in ref. 9). (These data behaved in the normal manner, i.e. as expected by the unmodified spreadsheet algorithm.)

TABLE 3

Cell contents for worksheet in Table 1

```
A1: [W10] "Alpha
B1: [W9] 'X(Time)
C1: [W7] ^N
D1: [W14] ^Y
E1: [W12] ^X*X
F1: [W10] ^X*Y
A2: [W10] \=
B2: [W9] \=
C2: [W7] \=
D2: [W14] \=
E2: [W12] \=
F2: [W10] \=
A3: (F3) [W10] 0.203
B3: (F1) [W9] 10
C3: (F3) [W7] 0.665
D3: (S2) [W14] (1-(1-A3)^(1-$N))
E3: (S2) [W12] +B3*B3
F3: [W10] +B3*D3
A4: (F3) [W10] 0.377
B4: (F1) [W9] 20
D4: (S2) [W14] (1-(1-A4)^(1-$N))
E4: (S2) [W12] +B4*B4
F4: [W10] +B4*D4
A5: (F3) [W10] 0.523
B5: (F1) [W9] 30
D5: (S2) [W14] (1-(1-A5)^(1-$N))
E5: (S2) [W12] +B5*B5
F5: [W10] +B5*D5
A6: (F3) [W10] 0.645
B6: (F1) [W9] 40
D6: (S2) [W14] (1-(1-A6)^(1-$N))
E6: (S2) [W12] +B6*B6
F6: [W10] +B6*D6
A7: (F3) [W10] 0.743
B7: (F1) [W9] 50
D7: (S2) [W14] (1-(1-A7)^(1-$N))
E7: (S2) [W12] +B7*B7
F7: [W10] +B7*D7
A8: (F3) [W10] 0.822
B8: (F1) [W9] 60
D8: (S2) [W14] (1-(1-A8)^(1-$N))
E8: (S2) [W12] +B8*B8
F8: [W10] +B8*D8
A9: (F3) [W10] 0.883
B9: (F1) [W9] 70
D9: (S2) [W14] (1-(1-A9)^(1-$N))
E9: (S2) [W12] +B9*B9
F9: [W10] +B9*D9
A10: [W10] \=
B10: [W9] \=
C10: [W7] \=
D10: (S2) [W14] \=
E10: (S2) [W12] \=
F10: [W10] \=
A11: [W10] 'TOTALS==>
B11: (F1) [W9] @SUM(X)
D11: (S2) [W14] @SUM(Y)
E11: (S2) [W12] @SUM(XX)
F11: (S2) [W10] @SUM(XY)
A12: [W10] \=
B12: [W9] \=
C12: [W7] \=
D12: [W14] \=
E12: [W12] \=
F12: [W10] \=
A13: [W10] ^AAA2
B13: [W9] ^AAA1
D13: [W14] "BX0
F13: [W10] ^Inc
A14: [W10] \=
B14: [W9] \=
C14: [W7] \=
D14: [W14] \=
E14: [W12] \=
F14: [W10] \=
A15: (S2) [W10] (@ROWS(Y)*SXY-SX*SY)/(@ROWS(Y)*SXX-(SX)^2)
B15: [W9] (SY/@ROWS(Y))-$AAA2*(SX/@ROWS(Y))
D15: (S2) [W14] 0.0000486108
F15: [W10] 0.0001
A16: [W10] \-
B16: [W9] \-
C16: [W7] \-
D16: [W14] \-
E16: [W12] \-
F16: [W10] \-
A17: [W10] "\a-->
B17: [W9] '{let n,0.1}~{let inc,0.1}~
B18: [W9] '{let bx0,100}~
A19: [W10] "\d-->
B19: [W9] '{goto}n~{let n,+n+inc}~
B20: [W9] '{if @abs(+aaa1)<@abs(bx0)}{let bx0,aaa1}~{branch \d}
B21: [W9] '{branch \b}
A22: [W10] "\b-->
B22: [W9] '{goto}n~{let n,+n-2*inc}~{let bx0,aaa1}~
B23: [W9] '{goto}inc~{let inc,+inc/10}~
B24: [W9] '{if +inc>.0009}{branch \d}
B25: [W9] '{goto}vals~
A27: [W10] 'Final values n & k =>
D27: (F3) [W14] +N
E27: (S2) [W12] (@ABS(+AAA2/(1-$N)))
```

Based on the above, it is also suggested that the unmodified particular spreadsheet algorithm in question used for NITG data be replaced by the more reliable modified algorithm described above.

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